Problem Set 2

1. (a) A heat-resistant polymer Nomex has a number-average molecular weight of 24,116. Hydrolysis of the polymer yields 39.31% by weight m-aminoaniline, 59.81% terephthalic acid, and 0.88% benzoic acid. Write the formula for this polymer. Calculate the degree of polymerization and the extent of reaction. (b) Calculate the effect on the degree of polymerization if the polymerization had been carried out with twice the amount of benzoic acid.

2. Calculate the feed ratio of adipic acid and hexamethylene diamine that should be employed to obtain a polyamide of approximately 15,000 molecular weight at 99.5% conversion. What is the identity of the end groups of this product? Do the same calculation for a 19,000-molecular-weight polymer.

3. What proportion of benzoic acid should be used with an equimolar mixture of adipic acid and hexamethylene diamine to produce a polymer of 10,000 molecular weight at 99.5% conversion? Do the same calculation for 19,000 and 28,000 molecular weight products.

4. Calculate the extent of reaction at which gelation occurs for the following mixtures:
a. Phthalic anhydride and glycerol in stoichiometric amounts.
b. Phthalic anhydride and glycerol in the molar ratio 1.500 : 0.980
c. Phthalic anhydride, glycerol, and ethylene glycol in the molar ratio 1.500 : 0.990 : 0.002
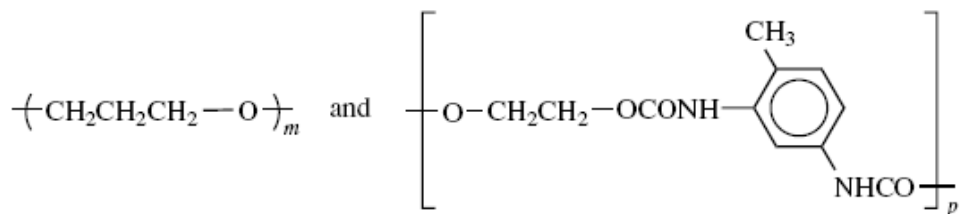d. Phthalic anhydride, glycerol, and ethylene glycol in the molar ratio 1.500 : 0.500 : 0.700
Describe the effect of unequal functional groups reactivity (e.g., for the hydroxyl groups in glycerol) on the extent of reaction at the gel point.

5. Describe by means of equations how random and block copolymers having the following compositions could be synthesized:
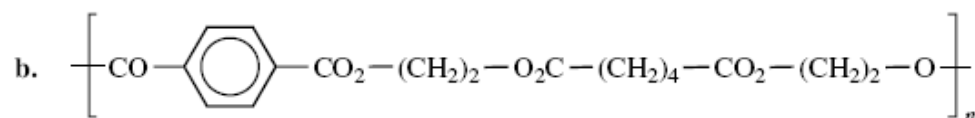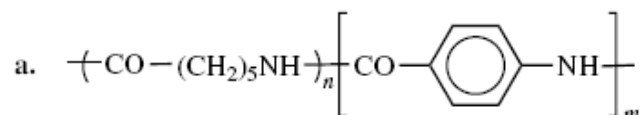
6. How would you synthesize a block copolymer having segments of the following structures?

$$+CH_2CH_2CH_2-O\!\!+_m \quad \text{and} \quad \left[O-CH_2CH_2-OCONH-\!\!\!\bigcirc\!\!\!-NHCO\right]_p$$

with CH_3 attached to the ring.

7. Using ^{14}C-labeled AIBN as an initiator, a sample of styrene is polymerized to a number-average degree of polymerization of 1.52×10^4. The AIBN has an activity of 9.81×10^7 counts min^{-1} mol^{-1} in a scintillation counter. If 3.22 g of the polystyrene has an activity of 203 counts min^{-1}, what is the mode of termination?

8. The following data were obtained in the thermal initiated bulk polymerization of monomer Z ([M]=8.3M) using radical initiator W at 60°C:

$R_p \times 10^3$ (mol L^{-1} s^{-1})	$\overline{X}_n$
0.0050	8350
0.010	5550
0.020	3330
0.050	1317
0.10	592
0.15	358

Calculate C_M, $k_p/k_t^{1/2}$, and fk_d in this polymerization if it is experimentally observed that $R_p = 4.0 \times 10^{-4}[I]^{1/2}$. Is chain transfer to initiator important? If it is, describe how to calculate C_I